INTERACTION OF LIGHT WITH MATTER

One of the most important topics in time-dependent quantum mechanics for chemists is the
description of spectroscopy. This refers to interrogating the properties and behavior of molecules
(matter) with light fields (electromagnetic radiation). We most often watch how matter changes
the properties of the incident light, but sometimes we also watch changes that the light field
induces in the matter (photochemistry).

Like every other problem we want to derive a Hamiltonian that we can use to describe the
interaction of an electromagnetic field with charged particles. We will show how an interaction
picture representation naturally emerges with:

\[ H = H_0 + V(t) = H_{\text{matter}} + H_{\text{light-matter}}(t) \]

Here the Hamiltonian for the light-matter interaction will be called the Electric Dipole
Hamiltonian.

Our approach to this problem will be semiclassical:

(1) Treat matter quantum mechanically

(2) Treat the field classically. This means that we don't account for how the field changes
as a result of the interaction. (Purely quantum mechanically we might expect to raise
the quantum state of the system and annihilate a photon from the field. We won't deal
with this right now).

We will develop a classical Hamiltonian for the interaction of charged particles with an
electromagnetic field and then substitute quantum operators for the matter.

\[ p \rightarrow -i\hbar \hat{\nabla}, \quad x \rightarrow \hat{x} \]
**Brief outline of electrodynamics**

(An outline of the derivation of the plane wave solutions to the fields and vector potential is described in the appendix. Also, see Jackson, *Classical Electrodynamics*, or Cohen-Tannoudji, et al., Appendix III.)

We need to work through two steps.

1. We need to know something about electromagnetic fields
2. We need to describe how an electromagnetic field interacts with charged particles.

> Maxwell’s Equations describe electric and magnetic fields \((E, B)\).

> To construct a Hamiltonian, we require a potential (rather than a field).

> To construct a potential representation of \(E\) and \(B\), you need a vector potential \(A(\vec{r}, t)\) and a scalar potential \(\phi(\vec{r}, t)\). For electrostatics we normally think of the field being related to the electrostatic potential through \(E = -\nabla \phi\), but for a time varying field, the electrodynamic potential is expressed in terms of both \(A\) and \(\phi\).

> In general an EM wave written in terms of the electric and magnetic fields requires 6 variables (the \(x, y, z\) components of \(E\) and \(B\)). This is an overdetermined problem; Maxwell’s equations constrain these. The potential representation has four variables \((A_x, A_y, A_z\) and \(\phi)\), but these are still not uniquely determined. We choose a constraint – a representation or guage – that allows us to uniquely describe the wave.

We choose a gauge such that \(\phi = 0\) (Coulomb gauge) which leads to plane-wave description of \(E\) and \(B\):

\[
-\nabla^2 A(\vec{r}, t) + \frac{1}{c^2} \frac{\partial^2 A(\vec{r}, t)}{\partial t^2} = 0
\]

\[
\nabla \cdot A = 0
\]

This wave equation allows the vector potential to be written as a set of plane waves:
\[
\vec{A}(\vec{r}, t) = A_0 \hat{\varepsilon} e^{i(\vec{k} \cdot \vec{r} - \omega t)} + A_0^* \hat{\varepsilon} e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \quad \text{(oscillates as cos } \omega t) 
\]

since \( \nabla \cdot \vec{A} = 0, \quad \vec{k} \cdot \hat{\varepsilon} = 0 \implies \vec{k} \perp \hat{\varepsilon} \) where \( \hat{\varepsilon} \) is the polarization direction of the vector potential.

\[
\vec{E} = -\frac{\partial \vec{A}}{\partial t} = i \omega A_0 \hat{\varepsilon} \left( e^{i(\vec{k} \cdot \vec{r} - \omega t)} - e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \right) 
\]

(oscillates as sin \( \omega t \))

\[
\vec{B} = \nabla \times \vec{A} = i \left( \frac{\vec{k} \times \vec{\varepsilon}}{|\vec{k}|} \right) A_0 \left( e^{i(\vec{k} \cdot \vec{r} - \omega t)} - e^{-i(\vec{k} \cdot \vec{r} - \omega t)} \right)
\]

\( \hat{b} = \hat{k} \times \hat{\varepsilon} \)

so we see that \( \hat{k} \perp \hat{\varepsilon} \perp \hat{b} \)

\( \hat{\varepsilon} \) is the direction of the electric field polarization and \( \hat{b} \) is the direction of the magnetic field polarization.

We define \( \frac{1}{2} E_0 = i \omega A_0 \)

\( \frac{1}{2} B_0 = i |\vec{k}| A_0 \quad \left( \frac{E_0}{B_0} = \frac{\omega}{|\vec{k}|} = c \right) \)

\[
\vec{E}(\vec{r}, t) = |E_0| \hat{\varepsilon} \sin (\vec{k} \cdot \vec{r} - \omega t)
\]

\[
\vec{B}(\vec{r}, t) = |B_0| \hat{b} \sin (\vec{k} \cdot \vec{r} - \omega t)
\]
**Hamiltonian for radiation field interacting with charged particle**

We will derive a Lagrangian for charged particle in field, then use it to determine classical Hamiltonian, then replace classical operators with quantum.

Start with Lorentz force on a charged particle:

\[ F = q \left( \mathbf{E} + \mathbf{v} \times \mathbf{B} \right) \]  

(1)

where \( \mathbf{v} = \dot{\mathbf{r}} \) is the velocity. In one direction \((x)\), we have:

\[ F_x = q \left( E_x + \dot{y} B_z - \dot{z} B_y \right) \]  

(2)

The generalized force for the components of the force in the \( x \) direction in Lagrangian Mechanics is:

\[ F_x = -\frac{\partial U}{\partial x} + \frac{d}{dt} \left( \frac{\partial U}{\partial \dot{x}} \right) \]  

(3)

\( U \) is the potential energy. Using our relationships for \( \mathbf{E} \) and \( \mathbf{B} \) in terms of \( A \) and \( \phi \) in eq. (2) and working it into the form of eq. (3), we can show that:

\[ U = q\phi - q\mathbf{v} \cdot \mathbf{A} \]  

(4)

See CTDL, app. III, p. 1492. Confirm by plugging into (3).

Now we can write a Lagrangian

\[ L = T - U \]

\[ = \frac{1}{2} m \mathbf{v}^2 + q\mathbf{v} \cdot \mathbf{A} - q\phi \]  

(5)

Now the Hamiltonian is related to the Lagrangian at:

\[ H = \mathbf{p} \cdot \mathbf{v} - L \]

\[ = \mathbf{p} \cdot \mathbf{v} - \frac{1}{2} m \mathbf{v}^2 - q \mathbf{v} \cdot \mathbf{A} - q\phi \]  

(6)

\[ \mathbf{p} = \frac{\partial L}{\partial \mathbf{v}} = m \mathbf{v} + q \mathbf{A} \quad \Rightarrow \quad \mathbf{v} = \frac{1}{m} \left( \mathbf{p} - q \mathbf{A} \right) \]  

(7)
Now substituting (7) into (6), we have:

\[ H = \frac{1}{m} \bar{p} \cdot (\bar{p} - q\bar{A}) - \frac{1}{2m} (\bar{p} - q\bar{A})^2 - \frac{q}{m} (\bar{p} - q\bar{A}) \cdot \bar{A} + q\varphi \]

\[ H = \frac{1}{2m} [\bar{p} - q\bar{A}(\bar{r}, t)]^2 + q\varphi(\bar{r}, t) \]

This is the classical Hamiltonian for a particle of charge \( q \) in an electromagnetic field. So, in the Coulomb gauge \( (\varphi = 0) \), we have the Hamiltonian for a collection of particles in the absence of an external field:

\[ H_0 = \sum_i \left( \frac{\bar{p}_i^2}{2m_i} + V_0(\bar{r}_i) \right) \]

and in the presence of the EM field:

\[ H = \sum_i \left( \frac{1}{2m_i} (\bar{p}_i - q_i \bar{A}(\bar{r}_i))^2 + V_0(\bar{r}_i) \right) \]

Expanding:

\[ H = H_0 - \sum_i \frac{q_i}{2m_i} (\bar{p}_i \cdot \bar{A} + \bar{A} \cdot \bar{p}_i) + \sum_i \frac{q_i}{2m_i} |\bar{A}|^2 \]

Generally the last term is considered small—energy of particles high relative to amplitude of potential—so we have:

\[ H = H_0 + V(t) \]

\[ V(t) = \sum_i \frac{q_i}{2m_i} (\bar{p}_i \cdot \bar{A} + \bar{A} \cdot \bar{p}_i) \]

Now we are in a position to substitute the quantum mechanical momentum for the classical:

\[ \bar{p} = -i\hbar \bar{\nabla} \]

\[ V(t) = \sum_i \frac{i\hbar}{2m_i} q_i (\bar{\nabla}_i \cdot \bar{A} + \bar{A} \cdot \bar{\nabla}_i) \]
We can show that \( \nabla \cdot \vec{A} = \vec{A} \cdot \nabla \). Notice \( \nabla \cdot \vec{A} = (\nabla \cdot \vec{A}) + \vec{A} \cdot \nabla \) (chain rule). For instance if we are operating on a wavefunction \( \nabla \cdot \vec{A} |\psi\rangle = (\nabla \cdot \vec{A}) |\psi\rangle + \vec{A} \cdot (\nabla |\psi\rangle) \), but we are working in the Coulomb gauge \( (\nabla \cdot \vec{A} = 0) \). Now we have:

\[
V(t) = \sum_i \frac{i \hbar q_i}{m_i} \vec{A} \cdot \vec{\nabla}_i
= -\sum_i \frac{q_i}{m_i} \vec{A} \cdot \vec{p}_i
\]

For a single charge particle our interaction Hamiltonian is

\[
V(t) = -\frac{q}{m} \vec{A} \cdot \vec{p}
\]

Using our plane-wave description of the vector potential:

\[
V(t) = -\frac{q}{m} \left[ A_0 \hat{e} \cdot \vec{p} e^{i(\vec{k} \cdot \vec{r} - \omega t)} + c.c. \right]
\]

**Electric Dipole Approximation**

If the wavelength of the field is much larger than the molecular dimension \((\lambda \rightarrow \infty) \) \(|k| \rightarrow 0 \), then \( e^{i\vec{k} \cdot \vec{r}} \rightarrow 1 \).

If \( r_0 \) is the center of mass of a molecule:

\[
|k| = \frac{2\pi}{\lambda}
\]

\[
e^{i\vec{k} \cdot \vec{r}} = e^{i\vec{k} \cdot \vec{r}_0} e^{i\vec{k} \cdot (\vec{r} - \vec{r}_0)}
= e^{i\vec{k} \cdot \vec{r}_0} \left[ 1 + i\vec{k} \cdot (\vec{r} - \vec{r}_0) + \ldots \right]
\]

For UV, visible, infrared—not X-ray—\(|k||\vec{r}_i - \vec{r}_0| < 1 \), set \( \vec{r}_0 = 0 \) \( e^{i\vec{k} \cdot \vec{r}} \rightarrow 1 \).

We do retain higher-order terms to describe higher order interactions with the field.

Retain second term for quadrupole transition moment: charge distribution interacting with gradient of electric field and magnetic dipole.
**Electric Dipole Hamiltonian**

\[
V(t) = \frac{-q}{m} A_0 \hat{\mathbf{p}} e^{-i\omega t} + c.c.
\]

Using \( A_0 = \frac{iE_0}{2\omega} \)

\[
V(t) = -\frac{iqE_0}{2m\omega} \left[ \hat{\mathbf{p}} e^{-i\omega t} - \hat{\mathbf{p}} e^{+i\omega t} \right]
\]

\[
V(t) = \frac{-qE_0}{m\omega} (\hat{\mathbf{p}} \cdot \mathbf{E}(t)) \sin \omega t
\]

or for a collection of charge particles (molecules):

\[
V(t) = - \left( \sum_i \frac{q_i}{m_i} (\hat{\mathbf{p}}) \right)^. \frac{E_0}{\omega} \sin \omega t
\]

**Harmonic Perturbation: Matrix Elements**

For a perturbation \( V(t) = V_0 \sin \omega t \) the rate of transitions induced by field is

\[
w_{k\ell} = \frac{\pi}{2\hbar} |V_{k\ell}|^2 \left[ \delta (E_k - E_\ell - \hbar \omega) + \delta (E_k - E_\ell + \hbar \omega) \right]
\]

Let’s look at the matrix elements for the E.D.H.

\[
V_{k\ell} = \langle k | V_0 | \ell \rangle = \frac{-qE_0}{m\omega} \langle k | \hat{\mathbf{p}} \rangle
\]

Evaluate the matrix element \( \langle k | \mathbf{p} | \ell \rangle \) using \( [\mathbf{p}, H_0] = \frac{i\hbar \mathbf{p}}{m} \)

\[
\langle k | \mathbf{p} | \ell \rangle = \frac{m}{i\hbar} \langle k | H_0 - H_0 \mathbf{p} | \ell \rangle
\]

\[
= \frac{m}{i\hbar} (\langle k | \mathbf{p} | \ell \rangle E_\ell - E_k \langle k | \mathbf{p} | \ell \rangle)
\]

\[
= im\omega_{k\ell} \langle k | \mathbf{p} | \ell \rangle
\]


\[
V_{kt} = -i q E_0 \frac{\omega_k}{\omega} \langle k | \hat{\varepsilon} \cdot \mathbf{r} | \ell \rangle
\]

or for a collection of particles

\[
V_{kt} = -i E_0 \frac{\omega_k}{\omega} \langle k | \hat{\varepsilon} \cdot \left( \sum_i q_i \mathbf{r}_i \right) | \ell \rangle = -i E_0 \frac{\omega_k}{\omega} \langle k | \hat{\varepsilon} \cdot \vec{\mu} | \ell \rangle
\]

\(\vec{\mu}\) is the dipole moment. More generally, we can write the dipole moment as the distribution of charge in the molecule:

\[
\vec{\mu} = \int d\mathbf{r} \ \rho(\mathbf{r})
\]

\[V(t) = -\vec{\mu} \cdot \mathbf{E}(t)\]

So the rate of transitions between quantum states induced by the electric field is

\[
w_{kt} = \frac{\pi}{2\hbar} |E_0|^2 \frac{\omega_{kt}^2}{\omega^2} \left| \left\langle k | \hat{\mu} \cdot \hat{\varepsilon} | \ell \right\rangle \right|^2 \left[ \delta(\omega_k - \omega_{kt} - \hbar \omega) + \delta(\omega_k - \omega_{kt} + \hbar \omega) \right] \\
\approx \frac{\pi}{\hbar^2} |E_0|^2 \left| \left\langle k | \hat{\mu} \cdot \hat{\varepsilon} | \ell \right\rangle \right|^2 \left[ \delta(\omega_{kt} - \omega) + \delta(\omega_{kt} + \omega) \right]
\]

This is an expression for the absorption spectrum since the rate of transitions can be related to the power absorbed from the field. More generally we would express the absorption spectrum in terms of a sum over all initial and final states – eigenstates of \(H_0\):

\[
w_{\beta} = \sum_{i,f} \frac{\pi}{\hbar^2} |E_0|^2 |\mu_{\beta f}|^2 \left[ \delta(\omega_{\beta f} - \omega) + \delta(\omega_{\beta f} + \omega) \right]
\]

The strength of interaction between light and matter is given by the matrix element

\(\mu_{\beta f} \equiv \langle f | \hat{\mu} \cdot \hat{\varepsilon} | i \rangle\). The scalar part \(\langle f | \mu | i \rangle\) says that you need a change of charge distribution between \(|f\rangle\) and \(|i\rangle\) to get effective absorption. This matrix element is the basis of selection rules based on the symmetry of the states. The vector part says that the light field must project onto the dipole moment. This allows information to be obtained on the orientation of molecules, and forms the basis of rotational transitions.
Relaxation Leads to Line-broadening

What happens to the probability of absorption if an excited state decays exponentially?

\[ |k\rangle \xrightarrow{\text{relaxes exponentially}} |n\rangle \]

... for instance by coupling to continuum

\[ P_k \propto \exp\left(-\omega_{nk} t\right) \]

First-order result:

\[ b_k = \frac{-i}{\hbar} \int_{t_0}^{t} d\tau \langle k | V | n \rangle \]

or \[ i\hbar \frac{\partial}{\partial t} b_k = e^{i\omega_{kl}t} V_{kl}(t) \]

If we add relaxation to description of \( b_k \), following the relationships we got when discussing relaxation:

\[ i\hbar \frac{\partial}{\partial t} b_k = e^{i\omega_{kl}t} V_{kl}(t) - \frac{\omega_{nk}}{2} b_k \]

Now we have

\[ \frac{\partial}{\partial t} b_k = \frac{-i}{\hbar} e^{i\omega_{kl}t} \sin \omega t V_{kl} - \frac{\omega_{nk}}{2} b_k(t) \]

\[ = \frac{E_0 \omega_{kl}}{2i\hbar \omega} \left[ e^{i(\omega t + \omega)} - e^{i(\omega t - \omega)} \right] \alpha_{kl} - \frac{\omega_{nk}}{2} b_k(t) \]

The solution to the differential equation

\[ \dot{y} + ay = b e^{int} \]

is
\[ y(t) = Ae^{-\alpha t} + \frac{b e^{i\omega t}}{a + i\alpha} \]

\[
b_k(t) = A e^{-\sigma_{\text{at}}/2} + \frac{E_0 \omega_{kl} \bar{\mu}_{kl}}{2i\hbar\omega} \left[ \frac{e^{i(\omega_{kl} + \omega)t}}{\bar{\omega}_{nk} / 2 + i(\omega_{kl} + \omega)} - \frac{e^{i(\omega_{kl} - \omega)t}}{\bar{\omega}_{nk} / 2 + i(\omega_{kl} - \omega)} \right]
\]

Let’s look at absorption only—long time limit:

\[
b_k(t) = \frac{E_0 \omega_{kl} \bar{\mu}_{kl}}{2i\hbar\omega} \left[ \frac{e^{i(\omega_{kl} - \omega)t}}{\omega_{kl} - \omega - i\bar{\omega}_{nk} / 2} \right]
\]

The probability of transition:

\[
P_k = |b_k|^2 = \left( \frac{E_0^2 |\mu_{kl}|^2}{4\hbar^2} \right) \frac{1}{(\omega_{kl} - \omega)^2 + \bar{\omega}_{nk}^2 / 4}
\]

Lorentzian lineshape:

The linewidth is related to the system rather than how we introduced the perturbation.

Linewidth related to relaxation dynamics.
Appendix: Review of Free Electromagnetic Field

Maxwell’s Equations (SI):

1. $\nabla \cdot \overrightarrow{B} = 0$
2. $\nabla \cdot \overrightarrow{E} = \rho / \varepsilon_0$
3. $\nabla \times \overrightarrow{E} = -\frac{\partial \overrightarrow{B}}{\partial t}$
4. $\nabla \times \overrightarrow{B} = \mu_0 \overrightarrow{J} + \varepsilon_0 \mu_0 \frac{\partial \overrightarrow{E}}{\partial t}$

$\overrightarrow{E}$: electric field; $\overrightarrow{B}$: magnetic field; $\overrightarrow{J}$: current density; $\rho$: charge density; $\varepsilon_0$: electrical permittivity; $\mu_0$: magnetic permittivity

We are interested in describing $\overrightarrow{E}$ and $\overrightarrow{B}$ in terms of a scalar and vector potential. This is required for our interaction Hamiltonian.

Generally: A vector field $\overrightarrow{F}$ assigns a vector to each point in space, and:

5. $\nabla \cdot \overrightarrow{F} = \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z}$ is a scalar

For a scalar field $\phi$

6. $\nabla \phi = \frac{\partial \phi}{\partial x} \hat{x} + \frac{\partial \phi}{\partial y} \hat{y} + \frac{\partial \phi}{\partial z} \hat{z}$ is a vector

where $\hat{x}^2 + \hat{y}^2 + \hat{z}^2 = \hat{r}^2$ unit vector

Also:

7. $\nabla \times \overrightarrow{F} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ F_x & F_y & F_z \end{vmatrix}$

Some useful identities from vector calculus are:

8. $\nabla \cdot (\nabla \times \overrightarrow{F}) = 0$

9. $\nabla \times (\nabla \phi) = 0$
\( \nabla \times (\nabla \times F) = \nabla (\nabla \cdot F) - \nabla^2 F \)

We now introduce a vector potential \( \vec{A}(\vec{r}, t) \) and a scalar potential \( \phi(\vec{r}, t) \), which we will relate to \( \vec{E} \) and \( \vec{B} \)

Since \( \nabla \cdot \vec{B} = 0 \) and \( \nabla (\nabla \times \vec{A}) = 0 \):

\( \vec{B} = \nabla \times \vec{A} \)

Using (3), we have:

\[ \nabla \times \vec{E} = -\nabla \times \frac{\partial \vec{A}}{\partial t} \]

or

\( \nabla \times \left[ \vec{E} + \frac{\partial \vec{A}}{\partial t} \right] = 0 \)

From (9), we see that a scalar product exists with:

\( \vec{E} + \frac{\partial \vec{A}}{\partial t} = -\nabla \varphi(\vec{r}, t) \)

or

\( \vec{E} = \frac{\partial \vec{A}}{\partial t} - \nabla \varphi \)

So we see that the potentials \( \vec{A} \) and \( \varphi \) determine the fields \( \vec{B} \) and \( \vec{E} \):

\( \vec{B}(\vec{r}, t) = \nabla \times \vec{A}(\vec{r}, t) \)

\( \vec{E}(\vec{r}, t) = -\nabla \varphi(\vec{r}, t) - \frac{\partial}{\partial t} \vec{A}(\vec{r}, t) \)

We are interested in determining the wave equation for \( \vec{A} \) and \( \varphi \). Using (15) and differentiating (16) and substituting into (4):

\( \nabla \times (\nabla \times \vec{A}) + \epsilon_0 \mu_0 \left( \frac{\partial^2 \vec{A}}{\partial t^2} + \nabla \frac{\partial \varphi}{\partial t} \right) = \mu_0 \vec{J} \)
Using (10):

\[
\left[ -\nabla^2 \vec{A} + \varepsilon_0 \mu_0 \frac{\partial^2 \vec{A}}{\partial t^2} \right] + \nabla \left( \nabla \cdot \vec{A} + \varepsilon_0 \mu_0 \frac{\partial \phi}{\partial t} \right) = \mu_0 J
\]

From (14), we have:

\[
\nabla \cdot \vec{E} = -\frac{\partial \nabla \cdot \vec{A}}{\partial t} - \nabla^2 \phi
\]

and using (2):

\[
-\frac{\partial \nu \cdot \vec{A}}{\partial t} - \nabla^2 \phi = \rho/\varepsilon_0
\]

Notice from (15) and (16) that we only need to specify four field components \((A_x, A_y, A_z, \phi)\) to determine all six \(\vec{E}\) and \(\vec{B}\) components. But \(\vec{E}\) and \(\vec{B}\) do not uniquely determine \(\vec{A}\) and \(\phi\). So, we can construct \(\vec{A}\) and \(\phi\) in any number of ways without changing \(\vec{E}\) and \(\vec{B}\). Notice that if we change \(\vec{A}\) by adding \(\nabla \chi\) where \(\chi\) is any function of \(r\) and \(t\), this won’t change \(\vec{B}\) \((\nabla \times (\nabla \cdot B) = 0)\). It will change \(E\) by \(-\frac{\partial \chi}{\partial t}:\nabla \chi\), but we can change \(\phi\) to \(\phi' = \phi - \frac{\partial \chi}{\partial t}\). Then \(\vec{E}\) and \(\vec{B}\) will both be unchanged. This property of changing representation (gauge) without changing \(\vec{E}\) and \(\vec{B}\) is gauge invariance. We can transform between gauges with:

\[
\vec{A}'(\vec{r}, t) = \vec{A}(\vec{r}, t) + \nabla \cdot \chi(\vec{r}, t)
\]

\[
\phi'(\vec{r}, t) = \phi(\vec{r}, t) - \frac{\partial}{\partial t} \chi(\vec{r}, t)
\]

Up to this point, \(A'\) and \(Q\) are undetermined. Let’s choose a \(\chi\) such that:

\[
\nabla \cdot \vec{A} + \varepsilon_0 \mu_0 \frac{\partial \phi}{\partial t} = 0
\]

Lorentz condition

then from (17):

\[
-\nabla^2 \vec{A} + \varepsilon_0 \mu_0 \frac{\partial^2 \vec{A}}{\partial t^2} = \mu_0 J
\]

The RHS can be set to zero for no currents.

From (19), we have:
Eqns. (23) and (24) are wave equations for $\vec{A}$ and $\varphi$. Within the Lorentz gauge, we can still arbitrarily add another $\chi$ (it must only satisfy (22)). If we substitute (20) and (21) into (24), we see:

\begin{equation}
\nabla^2 \chi - \varepsilon_0 \mu_0 \frac{\partial^2 \chi}{\partial t^2} = 0
\end{equation}

So we can make further choices/constraints on $\vec{A}$ and $\varphi$ as long as it obeys (25).

For a field far from charges and currents, $J = 0$ and $\rho = 0$.

\begin{equation}
-\nabla^2 A + \varepsilon_0 \mu_0 \frac{\partial^2 A}{\partial t^2} = 0
\end{equation}

\begin{equation}
-\nabla^2 \varphi + \varepsilon_0 \mu_0 \frac{\partial^2 \varphi}{\partial t^2} = 0
\end{equation}

We now choose $\varphi = 0$ (Coulomb gauge), and from (22) we see:

\begin{equation}
\nabla \cdot \vec{A} = 0
\end{equation}

So, the wave equation for our vector potential is:

\begin{equation}
-\nabla^2 A + \varepsilon_0 \mu_0 \frac{\partial^2 A}{\partial t^2} = 0
\end{equation}

The solutions to this equation are plane waves.

\begin{equation}
A = A_0 \sin(\omega t - \vec{k} \cdot \vec{r} + \alpha)
\end{equation}

\begin{equation}
A = A_0 \cos(\omega t - \vec{k} \cdot \vec{r} + \alpha')
\end{equation}

\(\alpha\): phase

$\vec{k}$ is the wave vector which points along the direction of propagation and has a magnitude:

\begin{equation}
k^2 = \omega^2 \mu_0 \varepsilon_0 = \omega^2 / c^2
\end{equation}

Since (28) $\nabla \cdot \vec{A} = 0$

\(-\vec{k} \cdot A_0 \cos(\omega t - \vec{k} \cdot \vec{r} + \alpha) = 0\)
(33) \[ \vec{k} \cdot \vec{A}_0 = 0 \quad \vec{k} \perp \vec{A}_0 \]

\( \vec{A}_0 \) is the direction of the potential \( \rightarrow \) polarization. From (15) and (16), we see that for \( \varphi = 0 \):

\[ \vec{E} = -\frac{\partial \vec{A}}{\partial t} = -\omega \vec{A}_0 \cos(\omega t - \vec{k} \cdot \vec{r} + \alpha) \]

\[ \vec{B} = \vec{\nabla} \times \vec{A} = -\left(\vec{k} \times \vec{A}_0\right) \cos(\omega t - \vec{k} \cdot \vec{r} + \alpha) \]

\[ \therefore \quad \vec{k} \perp \vec{E} \perp \vec{B} \]